Optimizing Steam Bubble Cavitation using Chemiluminescence

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ABSTRACT

Water treatment methods in the United States are constantly under development to help create more efficient, sustainable, and improved technologies. This is important as our water supply becomes ever more exposed to pharmaceuticals and personal care products (PPCPs). In the long term, the effects of these contaminants on the population are unknown. Today, many are pushing for more advanced treatment processes that can treat for PPCPs. Such processes are known as advanced oxidation processes (AOPs). One emerging AOP is the use of cavitation. Cavitation in particular has recently become of interest due to its ability to create hydroxyl radicals. During cavitation, the formation and collapse of microbubbles creates a volatile environment in which hydroxyl radicals are formed. Hydroxyl radicals are desirable because of their ability to aid in water treatment by destroying organic contaminants. One of the latest cavitation techniques in development is steam bubble cavitation. Other cavitation techniques are limited in their water treatment capabilities, but a recent study has suggested that steam bubble cavitation is more feasible due to its energy efficiency. Using a chemiluminescent reaction to document the zone of cavitation, a better understanding of hydroxyl radical formation could be gained. The goals of this research were: (1) to successfully create a steam bubble cavitation reactor and (2) quantify the formation and collapse of steam bubbles through the use of photography and chemiluminescence. At this time, these photographic and chemiluminescence techniques have not yielded conclusive results. However, similar steam cavitation research has returned promising results, warranting further study of this novel water treatment technology using chemiluminescence.

INTRODUCTION

Overview

In the United States, industrial pollution of the environment has become a tragic problem. Contaminants from the manufacture and use of everyday household products and pharmaceuticals are constantly being added to our water systems. The task of removing these contaminants from streams and groundwater in an economically and environmentally sustainable manner is challenging. Traditional techniques to treat toxic and hazardous materials include incineration, landfilling, biological activity, and chemical treatment. Techniques, such as landfilling, only transfer contaminants to another location or phase; while other techniques, such as biodegradation, are often unpredictable, uneconomical, and slow to process (Adewuyi, 2005). The need for sustainable treatment methods is apparent and urgent. The newest studies involve oxygen-based processes, referred to as advanced oxidation processes (AOPs). These AOPs produce hydroxyl radicals in high quantities. After an AOP treatment is complete, final products of treatment are typically less toxic and easier to biodegrade than traditional methods (Adewuyi, 2005).

One emerging AOP uses high powered ultrasound to generate cavitation. While this method produces results, there are some drawbacks. The current state-of-the-art processes for generating ultrasound are considered to be energy intensive and inefficient compared to other AOPs. This study explored the use of steam as an energy source to create cavitation. Cavitation produced from ultrasound currently has an efficiency rate of about 9%. Steam bubble cavitation, however, is anticipated to have efficiency upwards of 85% (Mahulkar, Bapat, & Pandit, 2008). After the steam bubbles are introduced to the water sample, they exist for a short period of time, on the order of microseconds. Upon collapse, the local pressure and temperature for a single

microbubble rise radically, up to and above 1000 atm and 5000 K, respectively (Adewuyi, 2005). This dramatic phenomenon is the origin of the desirable hydroxyl radical. Due to its ability to readily reduce and oxidize other molecules, the hydroxyl radical has a short lifespan compared to other radicals and is highly reactive (Elia, Azoulay, & Zeiri, 2011). Figure 1 contains a conceptual diagram of a steam bubble collapsing.

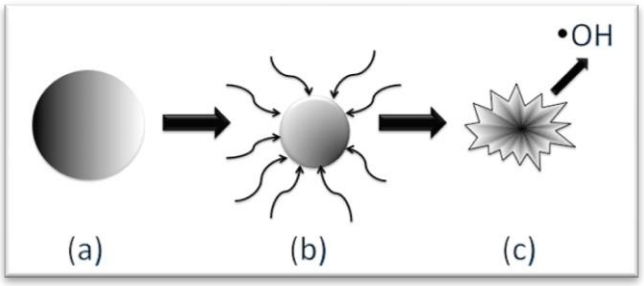

Figure 1: Steam bubble collapse. From (a) to (b), the steam bubble is immersed into subcooled water, where condensation of steam occurs due to the temperature difference and causes the bubble to shrink. As the bubble wall implodes (c), inertial forces compress the remaining gas inside the bubble, resulting in heating of the gaseous water; this heating causes the subsequent formation of hydroxyl radicals (•OH). Courtesy of E. Marron

This project was done in an attempt to understand bubble formation and collapse spatiality caused by steam bubble cavitation. Other research has shown that, upon collapse, free radicals react inside the bubble at the bubble/liquid interface and in the surrounding liquid. After the bubble's collapse, the radicals produced either react with surrounding radicals or diffuse into the water pool (Adewuyi, 2005). Therefore, the size of the bubbles before and at the moment of collapse should be related to the relative success of the cavitation. The initial hypothesis of the study was that larger cavitation bubbles would generate more hydroxyl radicals due to the greater amount of water vapor from steam condensing on the bubble wall.

The collapse of a cavitation bubble occurs on a size and time scale outside of human perception. The bubbles are on the order of micrometers in diameter, plus they form and

collapse in a matter of microseconds (Mahulkar, Bapat, & Pandit, 2008). Because of this, the exact moment and location of collapse cannot be observed with the naked eye. This study opted to study the cavitation phenomenon using chemiluminescence. Cavitation may be observed by using a chemical reaction in which a luminescing effect is created. The use of chemiluminescence in experimentation has several advantages including lower detection limits and enhanced sensitivity (Hu, Zhang, & Yang, 2008). The creation of hydroxyl radicals can be monitored through the fluorescence of luminol, which is produced by the reaction of hydroxyl radicals and another compound (Hirakawa, Yawata, & Nosaka, 2007). This study was done in an attempt to image the light emissions from such a reaction. It is also known that the concentration of hydroxyl radicals is related to the intensity of light emissions from the luminol (McMurray & Wilson, 1999). By analyzing gray level images taken during steam bubble cavitation during luminol reactions, a relationship could be developed to determine quantities of hydroxyl radical formed.

As the use of steam bubble cavitation is still under development, the primary purpose of this study was to design and build a steam bubble cavitation reactor and to document the progress of cavitation through images of chemiluminescence. The use of steam bubble cavitation as a water treatment tool carries great potential in its abilities to form hydroxyl radical in high amounts but to also be energy efficient, desirable qualities of a novel water treatment technology.

Objectives

The purposes of this study were to: (1) use photography to image the size of steam cavitation from formation to collapse, (2) use chemiluminescence techniques to determine the

spatial distribution and location of the steam bubble cavitation collapse, and (3) explore the effect of nozzle diameter and pool water temperature on bubble size, collapse location, and spatial distribution and relative levels of hydroxyl radical formation. This project was part of a larger project to explore the potential of steam bubble cavitation as a novel AOP within the research group of Dr. Linda Weavers of The Ohio State University and visiting professor Dr. Meiqiang Cai of Zhejiang Gongshang University.

MATERIALS AND METHODS

Experimental Setup

The traditional method of creating steam bubbles contains several processes and items, such as motors and pumps, all of which use energy. The total efficiency of this method is about 22% (Mahulkar, Bapat, & Pandit, 2008). Eliminating everything but a boiler results in a higher efficiency rate, and is much simpler all around. The essential components included in the testing apparatus were the sample volume reactor, steam boiler, cooling bath, and photo acquisition device. A simple diagram of these components can be seen in Figure 2. The steam boiler used can be seen in Figure 3. This boiler (Figure 3) consisted of a modified commercial pressure cooker (Fagor Duo Pressure Cooker) which was heated using a commercial grade hot plate (1300-Watt Waring Pro Single Burner). To use the pressure cooker as a steam boiler, several modifications were made to the pressure cooker lid. The modifications to the pressure cooker lid consisted of a temperature and pressure gauge, and two steam release valves – one for steam injection into the reactor and another for pressure control. The nozzle used for steam injection was a needle attached using a luer-lock fitting (Hamilton Metal Hub Needles). The steam then entered the sample volume through a small diameter needle (sizes 0.41, 0.60, 0.84 mm). To keep the sample volume at a cool temperature, a cooling bath circulated chilled water (10-15ºC) in a water jacket. These needle sizes and temperature were used based off promising results from a similar project within the research group. The reactor can be seen up close in Figure 4. This reactor had a total volume of 25 milliliters and keeps the solution cool using a water jacket. The complete initial experimental setup can be seen in Figure 5.

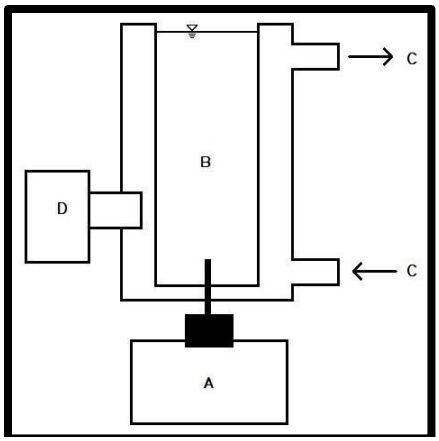

Figure 2: Initial design - (A) Steam boiler, (B) Reactor volume, (C) Cool circulating water, and (D) photo acquisition device.

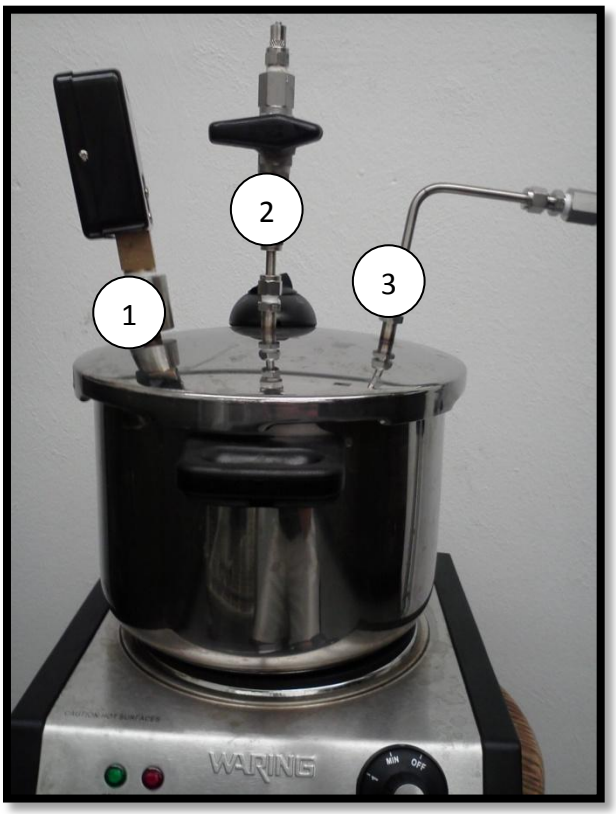

Figure 3: Modified Pressure Cooker with (1) pressure/temperature gauge, (2) steam release valve leading to reactor, and (3) control valve. The pressure cooker sits on a hot plate.

Figure 4: Image of reactor with water jacket, and steam injection needle.

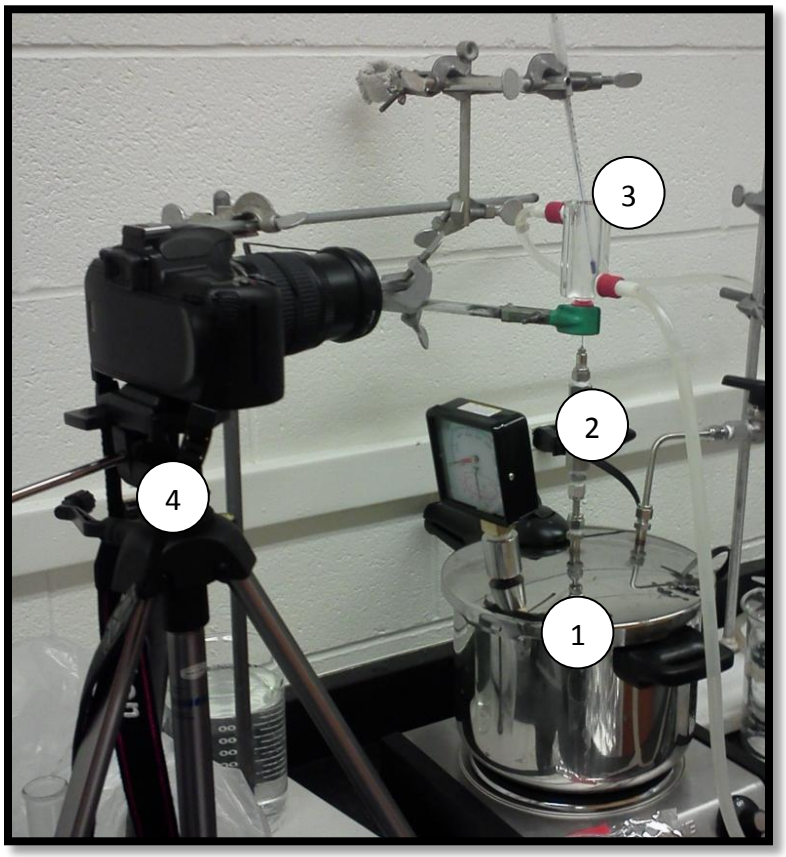

Figure 5: Modified pressure cooker (1) that sits on a hot plate. Attached to pressure cooker is a steam release valve (2), which is inserted into the bottom of the reactor (3). The reactor has a cool water jacket, which is connected to a cool water bath (out of frame). In the foreground is the Nikon camera that was used for imaging (4).

Due to limitations of temperature control and size of the reactor, a second experimental setup was used. The second setup utilized a Cole-Parmer Masterflex L/S peristaltic pump to draw the reactor fluid (Figure 4) out for additional cooling and storage. To prevent contamination or absorbance of the chemicals into the tubing, a Masterflex Precision FDA Viton Tubing was used. Seen in Figure 6 is a diagram of the fluid flow. For further cooling purposes, the temperature of the cooling bath was set at 10ºC and a glass coil was attached to the tubing to be inserted into the cooling bath. The outside storage allowed the volume of reactor solution to be expanded from 25 milliliters to over 350 milliliters. The reactor fluid was pumped through the cooling coil and into the top of this additional container (Figure 7). Fluids then drained via gravity back into the reactor (Figure 4). Based off information from within the research group, it was noted that there was heat loss through the nozzle. To counteract this heat loss, the needle was insulated using Septa (Figure 8).

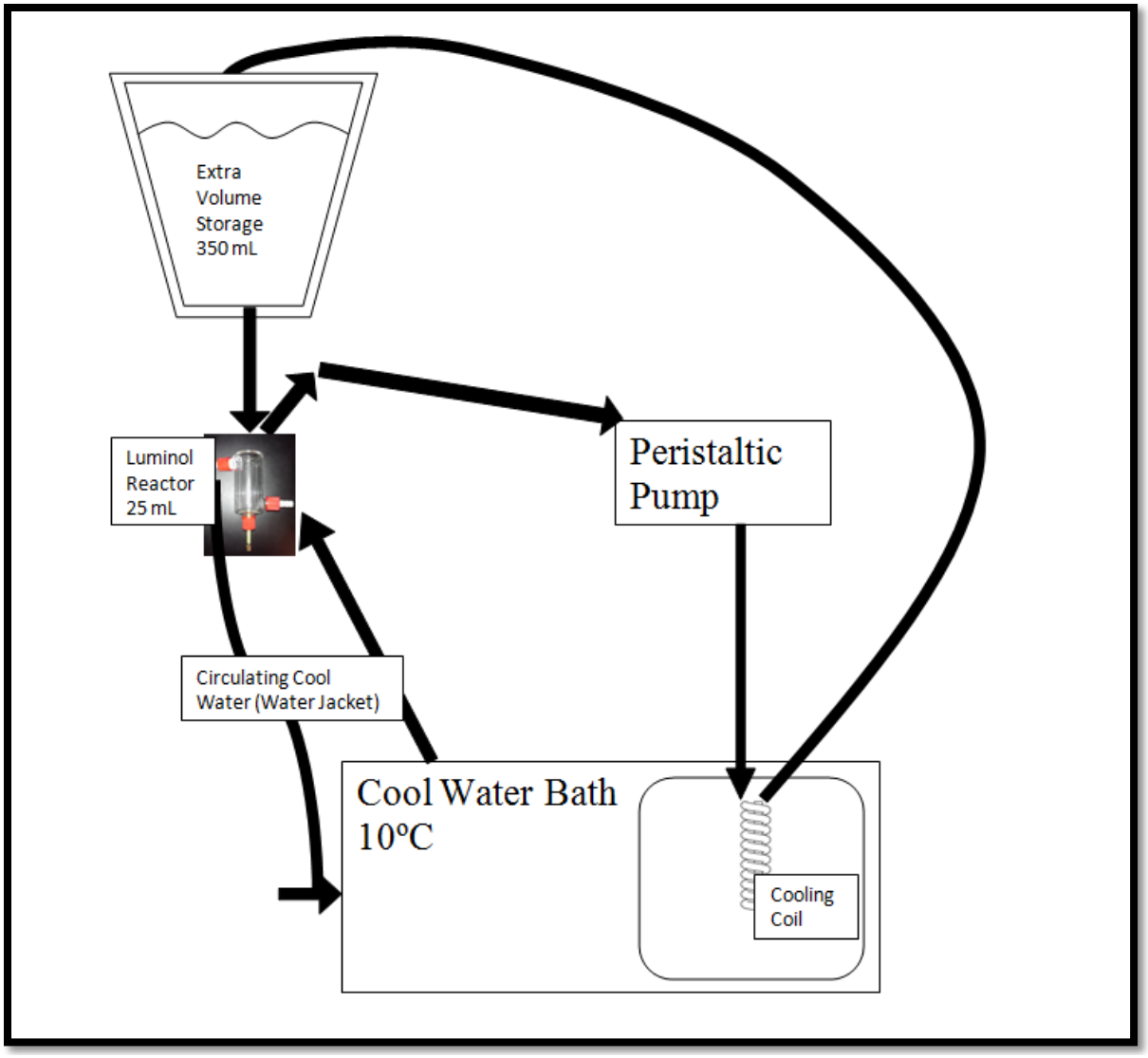

Figure 6: Schematic of second experimental setup

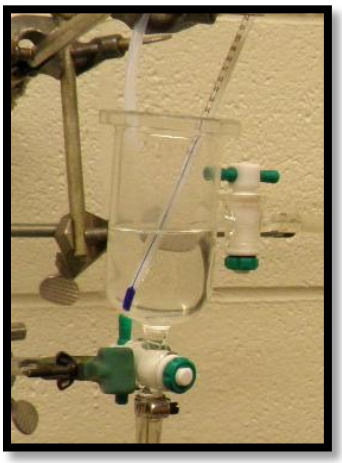

Figure 7: Image of reactor storage container.

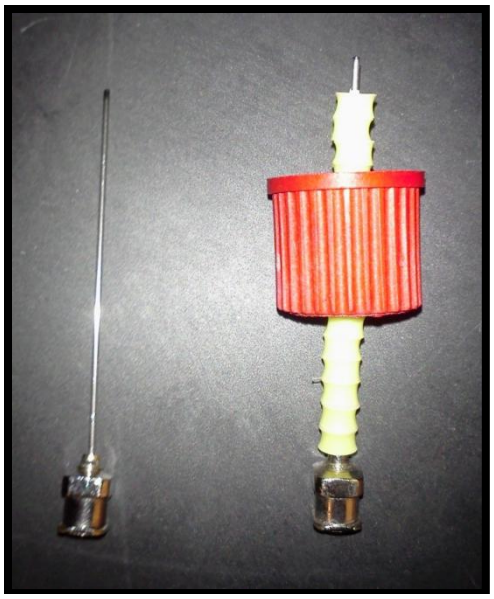

Figure 8: Image of needle (Left) and needle insulted with Septa (right)

To capture images, a Nikon N90S camera equipped with a AF Micro-Nikkor 105 mm f/2.8D lens was used. The camera was positioned on a tripod and the lens was left open for varying amounts of time during the experiment. Films used were Kodak TMax Black & White 100 and 400, and Fuji color 100.

Experimental Methods

When exposed to hydroxyl radicals, luminol (3-aminophthalhydrazide, 97%) forms a chemiluminescent product near the source of the hydroxyl radical (i.e., the cavitation bubbles). The luminol solution was made to be 0.001 M and the pH of the solution was adjusted to pH 11 with sodium hydroxide (pellets), based off procedures found in McMurray & Wilson (1999). For the experiments, the original concentration was used, as well as a concentrated solution. The concentrated solution was created using half the water required to reach 0.001 M. This was done to account for the steam flux as the experiment progressed. The goal was to have the steam-induced cavitation initiate the reaction that would trigger chemiluminescence of the luminol.

The intensity of the reaction would then be used to determine the spatial distribution of the cavitation zone (Chen, Weavers, & Walker, 206).

For each experiment, the steam boiler was filled with deionized water, then heated to 115ºC and pressurized to 110 kP (±5 kPa). Then 100 milliliters of the luminol solution was added to the reactor before opening the steam valve to allow the solution to cool to 10ºC. For all experiments, the steam valve was opened completely to allow steam to enter the reactor through the needle and the control valve was left closed to maintain temperature and pressure. The needles used were 0.60 and 0.84 mm in diameter. It was found that the 0.41 mm needle did not create a proper water-tight seal with the luer-lock fitting that attached the needle to the steam boiler, therefore it was not used. Before opening the valve, the lights were turned off and the camera's lens was opened. Images were captured for varying lengths of time at varying times during any one experiment. This was done in an attempt to document chemiluminescence at the commencement of cavitation, and subsequent changes in chemiluminescence as the experiment continued. Figure 9 shows exposure times and lengths used during experiments for a complete roll of film. For the initial and secondary experimental setups, three rolls of film were used, two color and one black and white.

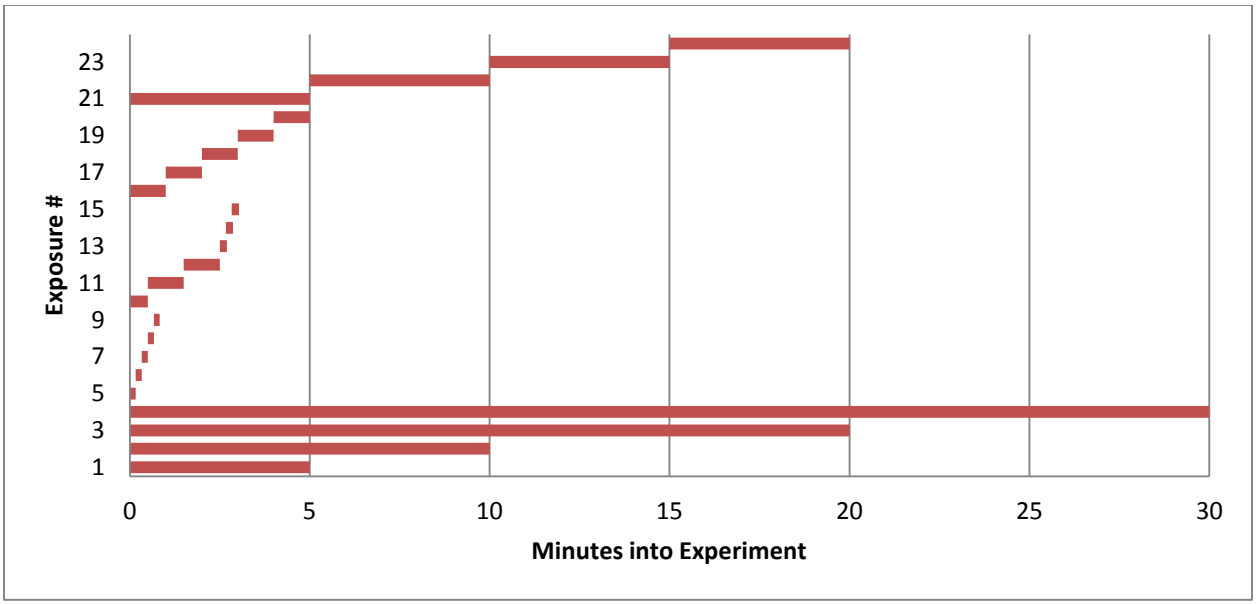

Figure 9: Graph showing exposure times and lengths

Analytical Methods

A complete experiment included bringing the steam reactor to temperature and refilling the reactor with new luminol solution. Once cooled, the steam valve was opened to allow the experiment to progress. It was during this time the camera was used. After completing several runs of the experiment, a roll of film would be full. The film was sent out to Cord Camera for processing. It was noted to the technicians that the images may be very faint; therefore the film was overexposed during developing.

RESULTS AND DISCUSSION

Initial Reactor Design and Redesign

As already mentioned, the first reactor design was inadequate because of limited cooling capabilities and volume of the reactor. The reactor had a maximum volume of 25 milliliters, while the steam flux with the medium sized needle was 3 milliliters per minute. Due to steam flux, the maximum reaction time was 5 minutes, whereas the desired time was up to 30 minutes. Due to the small volume and quick influx of steam, the temperature would quickly rise as well. Figure 10 shows a temperature curve in the first 5 minutes for the initial design. The 60ºC temperature and the 5 minute reaction time were not ideal for this experiment. To ensure the reaction of luminol under the conditions researched, the reactor was modified to create more ideal conditions, specifically significantly better temperature control and a much larger volume capacity.

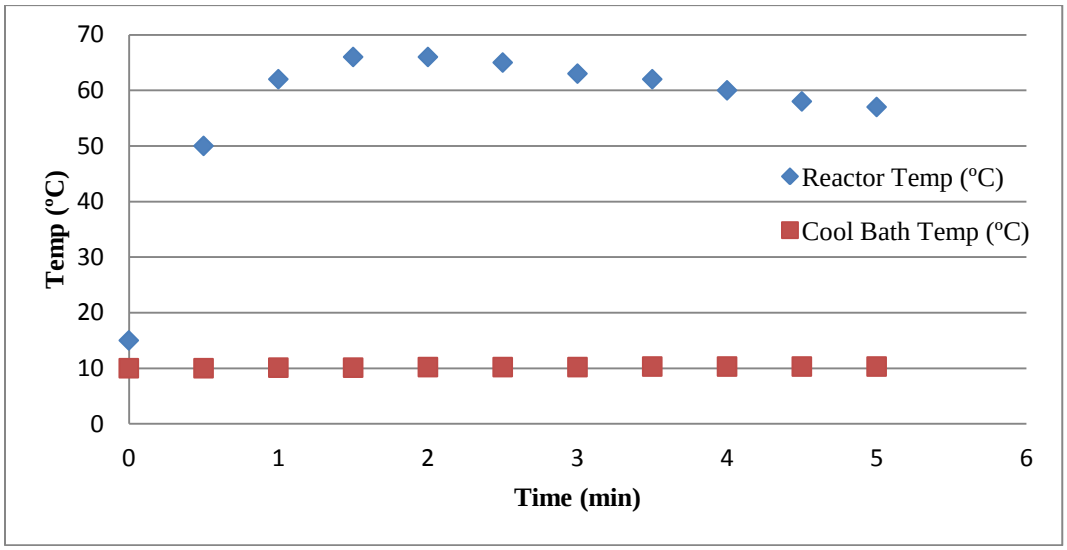

Figure 10: Temperature curve of initial experimental setup

After modifying the reactor to include the outside cooling and volume as previously mentioned, it was much more versatile. The setup was able to keep the reactor temperature under 30ºC over a period of 60 minutes (see Figure 11). With the new setup, the experiment was

continued using the luminol solution and was filmed using various film types and times. After developing, the film contained no images or any significant results to show chemiluminescence.

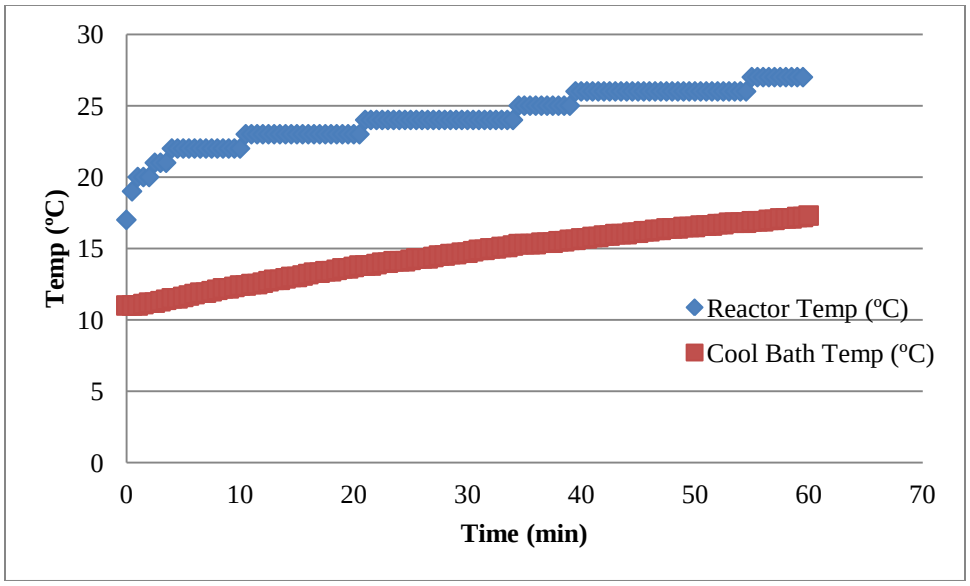

Figure 11: Temperature curve of second experimental setup

Future Work

At this time, images of chemiluminescence have not been captured using either of the experimental setups under any of the conditions created. As there have been promising results within the research group, it is advisable to continue to develop the reactor design. A reactor that circulates the cooling bath and the reactor solution for effective cooling is necessary. The temperature difference between the steam and the cool solution is thought to help drive the cavitation process. Therefore ensuring that the reactor solution temperature remains cold is essential. The reactor should also be more camera friendly, that is, should be resistant to condensation and have angles in the window that prevent reflections. Utilizing advanced camera settings or a more advanced camera may be able to help capture images of chemiluminescence.

CONCLUSIONS

This study was part of an ongoing process to explore the use of steam bubble cavitation as a novel AOP. The goal was to use a luminol solution that would react with the hydroxyl radicals generated from steam induced cavitation. In the presence of hydroxyl radicals, luminol can generate light that could be imaged with a camera, describing the quantity of the desirable compound. After experimenting with several reactors and environmental settings, no significant progress was made to describe steam bubble cavitation using chemiluminescence. With a new reactor that could improve on several aspects of the experimental setup, including temperature and shape, further research could be performed to continue to explore the use of chemiluminescence as a means to understand steam bubble cavitation. As other methods of experiment have produced promising results, addition research is recommended as to fully explore the use of steam bubble cavitation.

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